Oxidative Dehydrogenation of Ethane with CO₂ over CrOₓ Catalysts Supported on Al₂O₃ modified by ZrO₂ and/or CeO₂

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Abstract: A series of Cr-containing catalysts (with Cr content corresponding to one theoretical monolayer) supported on Al₂O₃, ZrO₂/Al₂O₃, CeO₂/Al₂O₃ and CeₓZr₁₋ₓO₂/Al₂O₃ was prepared using the impregnation techniques. The catalysts are characterized by the low-temperature N₂ sorption, XRD, TPR, UV-vis spectroscopy and tested in oxidative dehydrogenation of ethane using CO₂ as an oxidant. The results of physical-chemical characterization show that chromium is located on the support surface in amorphous Cr(VI) state. The addition of ZrO₂ and/or CeO₂ to the alumina support leads to increased activity in both the direct and the oxidative dehydrogenation reactions.

Keywords: oxidative dehydrogenation, ethane, carbon dioxide as an oxidant, chromia

1. Introduction

Ethylene, propylene and isobutylene are important building blocks in organic and polymeric synthesis in chemical and petrochemical industry. A growing demand in olefins requires new technologies in addition to traditional steam and catalytic cracking methods of olefin production. Catalytic dehydrogenation of alkanes is one of the most promising ways to obtain olefins among the new alternative routes due to high purity of the produced olefin. However, thermodynamic limitations make it difficult to carry out the direct dehydrogenation of ethane with high yield and selectivity towards ethylene. To avoid such limitations and shift the equilibrium towards the formation of target products, the oxidative dehydrogenation (ODH) of ethane is proposed by several scientific groups. Oxygen or carbon dioxide are used as oxidants. The prospects of using CO₂ as a mild oxidant are caused by the absence of deep oxidation, high selectivity to target olefin and utilization of CO₂ as a resource.

The reaction pathway in ODH using CO₂ is known to depend strongly on the support nature. According to our previous results, Cr-containing catalysts supported on γ-Al₂O₃ and ZrO₂ showed the highest rates of C₂H₄ formation (mmol·h⁻¹·g⁻¹) via ODH-CO₂ of ethane in comparison with those over CrO₃/Al₂O₃ and CrO₃/CeₓZr₁₋ₓO₂ samples. Taking into account the range of products and their stoichiometry, the following reactions set was proposed:

selective ODH: C₂H₆ + CO₂ ↔ C₂H₄ + CO + H₂O
direct dehydrogenation: C₂H₆ ↔ C₂H₄ + H₂
non-selective reaction: C₂H₆ + 5CO₂ ↔ 7CO + 3H₂O
water-gas shift reaction (RWGS): CO₂ + H₂ ↔ CO + H₂O
cracking: C₂H₆ ↔ 2CH₄
dry reforming: C₂H₆ + 2CO₂ ↔ 4CO + 3H₂

However, for CrO₃/Al₂O₃ catalyst the process consisted of two main reactions: direct dehydrogenation and RWGS, while for CrO₃/ZrO₂ sample ethylene was mainly formed through selective ODH. CrO₃/Al₂O₃ and CrO₃/CeₓZr₁₋ₓO₂ catalysts were characterized by lower ethylene formation rate due to high contribution of non-selective reactions of ethane transformation along with selective ODH. Thus, the combination of support properties can be used to design effective catalysts for ethane ODH with CO₂.

The purpose of the present work is to study the effect of ZrO₂ and/or CeO₂ addition on the state of the active component in CrO₃/Al₂O₃ catalysts and its activity in ODH-CO₂ of ethane.

2. Experimental

Initial γ-Al₂O₃ support was obtained by thermal decomposition of AIO(OH). ZrO₂ and/or CeO₂ modified γ-Al₂O₃ supports were prepared by incipient wetness impregnation technique using water solutions of ZrO(NO₃)₂·2H₂O and/or Ce(NO₃)₃·6H₂O stabilized by citric acid with ZrO₂ and/or CeO₂ contents of 2.5 atZr(Ce)/nm². The supports were dried at 80 °C overnight and calcined at 600 °C for 4 h. Cr-containing
catalysts with Cr loading corresponding to a monolayer (5 at% nm²) were prepared by incipient wetness impregnation of γ-Al₂O₃, ZrO₂/Al₂O₃, CeO₂/Al₂O₃ and CeₓZr₁₋ₓO₂/Al₂O₃ using aqueous solution of H₂CrO₄. The catalysts were dried at room temperature for 12 h and calcined at 600 °C for 4 h. The supports and catalysts were characterized by low-temperature N₂ sorption, XRD, TPR, UV-vis spectroscopy and tested in a fixed-bed reactor in oxidative dehydrogenation of ethane with CO₂ between 500 and 700 °C in consecutive incremental steps of 50°C.

3. Results and discussion
The study of the porous structure showed that all samples were mesoporous and the specific surface areas varied in the ranges of 146-201 and 132-159 m²/g for supports and catalysts, respectively. The absence of reflexes of Cr-containing phases in XRD patterns for all catalysts indicates highly dispersed state of CrOₓ on the surface of the supports. However, the reflexes of cubic phases of ceria and mixed cerium–zirconium oxides were found for catalysts modified by CeO₂ and CeₓZr₁₋ₓO₂. The DRS results indicated formation of Cr⁶⁺ state, the adsorption bands of Cr⁴⁺ were not observed. It was shown by TPR-H₂ that the addition of ZrO₂ and/or CeO₂ influenced on the reducibility of Cr⁶⁺.

The specific formation rates of C₂H₄, CO and CH₄ during the ODH-CO₂ for all catalysts are shown in Figure 1. Modification of the support of CrO₂/Al₂O₃ catalyst leads to changing of C₂H₄/CO ratio and decreasing of amount of by-products (CH₄ and coke). The CrO₂/ZrO₂/Al₂O₃ catalyst showed the highest activity in ODH-CO₂ of ethane. Addition of ZrO₂ caused the increase of ethylene formation rate and the decrease of that of CO as compared to unmodified CrO₂/Al₂O₃. The highest formation rate of CO and the lowest one of C₂H₄ are observed for CeO₂-modified catalyst. The modification by CeₓZr₁₋ₓO₂ did not lead to changing of ethylene formation rate. The addition of ZrO₂ and/or CeO₂ also leads to decrease of coke deposition on the catalyst surface.

4. Conclusions
All the studied catalysts mainly contain chromium in the Cr⁶⁺ state. The direct DH of ethane and RWGS is the main route over CrO₂/Al₂O₃, with cracking and coke formation as side reactions. Addition of ZrO₂ and/or CeO₂ to CrO₂/Al₂O₃ catalysts led to a decrease in coke formation. These changes in the main reactions can be ascribed to the differences in the chromium reducibility caused by its interaction with the support.

References